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Chemical transport modeling of potential atmospheric CO_2 sinks

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Abstract

The potential for carbon dioxide (CO_2) sequestration via engineered chemical sinks is investigated using a three dimensional chemical transport model (CTM). Meteorological and chemical constraints for flat or vertical systems that would absorb CO_2 from the atmosphere, as well as an example chemical system of calcium hydroxide ($Ca(OH)_2$) proposed by Elliott et al. [Compensation of atmospheric CO_2 buildup through engineered chemical sinkage, Geophys. Res. Lett. 28 (2001) 1235] are reviewed. The CTM examines land based deposition sinks, with $4° \times 5°$ latitude/longitude resolution at various locations, and deposition velocities (v). A maximum uptake of ~20 Gton (10^{15} g) C yr^{-1} is attainable with $v > 5$ cm s^{-1} at a mid-latitude site. The atmospheric increase of CO_2 (3 Gton yr^{-1}) can be balanced by an engineered sink with an area of no more than 75,000 km^2 at v of 1 cm s^{-1}. By building the sink upwards or splitting this area into narrow elements can reduce the active area by more than an order of magnitude as discussed in Dubey et al. [31].

Keywords: Carbon dioxide; Modeling; Sequestration

1. Introduction

It is likely that the observed global warming over the past 50 years is the result of the increase of greenhouse gas concentrations [2]. Carbon dioxide (CO_2) is an efficient greenhouse gas with a positive radiative absorption of about 1.5 W m^{-2} [2]. Its atmospheric concentration has increased by 0.4% (1.5 ppmv) annually during the past two decades and by 31% since 1750 [2]. Most of this

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increase is anthropogenic, from the burning of fossil fuels (6 Gton yr^{-1}). The ocean and land absorb about half of these emissions, while the other half corresponds to the atmospheric increase (3 Gton yr^{-1}). Carbon cycle models project that CO_2 will increase from its present concentration of 360 ppmv to over 500 ppmv by the year 2100 [2].

Reduction in anthropogenic CO_2 levels may counteract the effects of global warming. The most obvious route is to reduce the amount of fossil fuel consumption, or using alternate sources of energy. This is an overwhelming task at the present time. Other options include scrubbing CO_2 at the source, or removal downwind of stationary sources [3,4]. Sequestration of CO_2 has been proposed in such reservoirs as the deep sea [5–9], aquifers, sediments [10,11] and soils [12]. Here, the reaction of carbonic acid via engineered chemical sinks, as proposed by Elliott et al. [1], is further explored. Using a chemical transport model (CTM), the sequestration potential of the proposed removal process is simulated. The thermodynamics and kinetics of an example chemical system are also reviewed.

2. Background

How adequately can perfect, flat absorbers extract CO_2 from the atmosphere? Meteorological transport and absorption rates must be considered to determine the size limits of the sink. First, imagine a strip of perfect absorber 100 km wide running north/south from pole to pole. A few generalizations can be made to facilitate the following calculations. The dominant global winds are geostrophic (above 1 km and not affected by shear stresses) and westerly (from west to east). Horizontal velocities are (on average) about 1, 10 and 30 m s^{-1}, for the surface, planetary boundary layer (up to 1 km) and free troposphere, respectively. Other transport characteristics are listed in Table 1. A parcel of air passing over the sink would lose CO_2 from the bottom up, and removal can be viewed as analogous to a serial resistance process. Steady state is achieved within local vertical mixing times. The residence time of the air above the sink would be 10^4 s in the lower atmosphere. The slow transfer step is transport through the laminar layer above the sink. Regarding the free troposphere as isolated, the sink can remove 10% of the CO_2 from the boundary layer during a single transit at a 1 cm s^{-1} transfer velocity. Backfilling from the free troposphere occurs within hours. When other factors, such as decreased turbulence at night, are included, the average removal may be 5% of the CO_2.

The boundary layer contains about one tenth of the total atmospheric mass of CO_2. One complete pass over the sink will absorb four out of the 750 Gton C [13] in the atmosphere. In one year, an air parcel at mid-latitudes will circulate 25 times around the globe [14]. The total loss of

Table 1
Vertical transport characteristics near the earth's surface [1]

	Laminar layer	Boundary layer	Free troposphere
Thickness (cm)	0.01–0.1	10^5	10^6
Diffusivity ($cm^2\ s^{-1}$)	0.1 (molecular)	10^6 in daytime	10^5
Transfer (cm s^{-1})	1–10	10 in daytime slow at night	0.1
Internal mixing (s)	0.001–0.1	10^4	10^7

CO_2 is almost 100 Gton C yr^{-1}, more than ten times greater than the anthropogenic, fossil fuel combustion input. Therefore, the sink can be reduced considerably in size. Ten percent of the pole to pole distance (~20,000 km) should be adequate. Now, imagine two rectangular sinks, 100 km wide, running 1000 km along a meridian, one in each hemisphere. The sinks remove CO_2 from the lowest kilometer as westerlies move across. Horizontal diffusivities are small (10^4 m^2 s^{-1}) at the surface [15], but air is replaced vertically, and latitudinal mixing takes two to three months.

Alternatively, a square area of 300×300 km^2 would suffice. In either case, the hundred thousand square kilometer value is an upper limit. If the sinks were not flat, but built upward, as fences or towers, this would further counteract laminarity restrictions. Roughness elements in the absorber would reduce the thickness of the molecular diffusion layer. A transfer velocity of 10 cm s^{-1} could possibly be approached. Structures as tall as 10 m and maintained over long horizontal distances are conceivable. The structure height is about 1% of the boundary layer height, and ten units would remove as much CO_2 as 100 km of flat material. However, these options may alter the momentum budget of the lower atmosphere. An alternative approach which greatly reduces the active area required by collection units is to split a large single unit into a large number of parallel units separated by substantial gaps in the prevailing direction of the wind [31]. The limitation of a single large unit is the mixing time of the atmosphere in the vertical direction. This creates a CO_2 depleted shadow downwind of the leading edge of the collection unit. The result is a significant reduction in the collection magnitude of the sink a short distance beyond its leading edge which limits the usefulness of most of the downwind part of the large single unit. By creating gaps between narrow units, nearly the same amount of CO_2 can be extracted over the same total surface area, but now the gaps are no longer covered by active absorption units. Instead the gaps simply provide a distance over which the air is vertically mixed thereby significantly replenishing the CO_2 in the near ground layer before it encounters the next active absorption unit. Micrometeorological modeling is being used to investigate these possibilities in detail [31]. Micrometeorological modeling would be necessary to investigate these possibilities.

3. Chemistry

A chemical system for CO_2 sequestration is shown in Table 2. It involves the aqueous reaction of CO_2 with $Ca(OH)_2$, a common basic substance. In this case, CO_2 acts like a weak acid and forms calcium carbonate ($CaCO_3$). Reaction 1 is spontaneous under ambient conditions. The CO_2 released in Reaction 2 must be captured, and the calcium must be recycled effectively. Reaction 2, however, becomes spontaneous only above ~1000 K. With proper insulation and heat exchange systems, the energy required may approach the endothermicity of Reaction 2. The overall

Table 2
Chemistry and selected thermodynamic properties (in kcal mol^{-1}) of a proposed chemically engineered CO_2 sink [1]

Reaction	$\Delta H°r \times n$	$\Delta G°r \times n$
(1) $CO_2(g) + Ca^{2+}(aq) + 2OH^-(aq) \rightarrow CaCO_3(s) + H_2O(l)$	−22.9	−24.8
(2) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	42.7	31.2
(3) $CaO(s) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$	−19.8	−6.4
Net null	0	0

objective is to concentrate atmospheric CO_2 (~360 ppmv) to one atmosphere of pressure. This reverse mixing process can be described as a free energy change and amounts to 5 kcal mol^{-1} over the costs of Table 2.

Gas to liquid diffusion must be considered also in this system. Rate constants for diffusion controlled bimolecular aqueous reactions are on the order of 10^{10} M^{-1} s^{-1}, and aqueous molecular diffusion coefficients are about 10^{-5} cm^2 s^{-1}. In a one dimensional diffusion model of the sink column, scale depths of a tenth of 1 μm (10^{-5} cm) and a piston velocity of several hundred centimetre per second are achievable for vertical transfer. In a basic solution, the reaction with OH^- is favored, and CO_3^{2-} is the most stable carbon species. Carbonate formation results when Ca^{2+} is the conjugate cation, with a solubility product of 10^{-8}. For the hydration (CO_2 + OH), the rate constant (k) is 10^4 M^{-1} s^{-1} and a scale depth of 1 μm is derived. The Henry's Law constant for CO_2 is close to unity in an alkaline solution. For a saturated reagent, piston velocities drop to the order of 0.1 cm s^{-1}.

Gas and liquid phase restrictions can be reduced by subjecting the air above the sink area to an aerosol spray of $Ca(OH)_2$. Using cloud properties [15] as a reference, if $Ca(OH)_2$ is present at 10^{-2} M (versus 10^{-5} M CO_2 in air), in 10^{-6} of the volume of an air parcel, Reaction 1 is reagent limited. If the particle size is designed to be 100 μm, in 1 l (1000 cm^{-3}), the volume ratio to the gas phase is $>10^{-3}$, and Ca^{2+} is available in excess. The particle surface area is 10^{-3} cm^2, and the total interface is 1 cm^2 cm^{-3}. The diffusion/reaction velocity is 0.1 cm s^{-1}, and the lifetime of CO_2(g) is 10 s. The particles settle at 100 cm s^{-1}. At a height of 10 m, the $Ca(OH)_2$ droplets absorb CO_2 and sediment in less than a minute. Laboratory uptake experiments of ambient air bubbled through saturated calcium hydroxide solutions in an impinger indicate that CO_2 collection efficiencies of order 50% can easily be obtained [31] for sustained periods of time, offering promise for this extraction scheme.

4. Model description and simulations

Chemical transport modeling of a perfect, flat CO_2 sink reinforces the crude analysis described above by using realistic time space varying winds and numerical integration of chemical loss. The University of California (UCI) CTM, adapted from Prather et al. [16], is used to solve the continuity equations for chemical species over a global three dimensional grid. A split operator method calculates the separate effects of dry and wet convection (heat transport), advection (horizontal convective transport), large scale diffusion, sources and chemistry. The grid resolution is 4° in latitude and 5° in longitude. The CTM contains nine vertical layers centered at pressure levels of 975, 909, 800, 645, 478, 328, 206, 112 and 40 mbar, with the upper two being stratospheric layers. The top layer serves as a rigid lid.

The Goddard Institute for Space Studies general circulation model II generates a globally self-consistent set of daily wind fields, convergences, convective fluxes, temperatures, humidities and cloud cover [17]. These data include 8 h averages of mass flux, pressure fields, convection frequencies and 5 day averages of temperature. The meteorological fields are recycled annually in the CTM, and therefore, interannual variation cannot be taken into account. The CTM is extensively documented for many tropospheric applications: CFCs [16], ^{85}Kr [18], CO_2 [19], ^{222}Rn [20,21], CH_3CCl_3 [22], CH_4 [23], ^{210}Pb [24] and continental O_3 [25,26].

The entire atmosphere is initialized with a mixing ratio of 360 ppmv CO_2, and one or more surface grid cells are selected for location of the artificial sink. The CO_2 sink is simulated as a deposition velocity loss process in the lowest (surface) layer of the CTM. The amount of CO_2 uptake depends on the amount of CO_2 in the bottom layer and the deposition velocity (v). Five different values of v are tested at one location (Nevada—118°W, 38°N): 0.1, 0.5, 1.0, 5.0 and 10.0 cm s^{-1}. The 'optimal' v is then used at three other surface locations: Gobi Desert (108°E, 50°N), Equatorial Pacific Ocean (178°W, 2°S) and the Antarctic (3°E, 82°S). Additionally, a two box sink with northern and southern hemisphere Pacific Ocean locations is used (178°W, 46°N and 46°S). These are plausible locations for an engineered sink based on sparse population and available space.

5. Results

The total amount of carbon captured over one year (Gton C yr^{-1}) in the CTM is calculated for six different v (Table 3). The maximum amount of carbon that can be absorbed is 19 Gton C yr^{-1}. This upper limit is achieved with $v > 5$ cm s^{-1}. At higher v, the loss becomes limited by the amount of CO_2 in the lowest grid box. At $v = 1$ cm s^{-1}, 7 Gton C yr^{-1} are absorbed, an amount about equal to the anthropogenic input. Thus, 1 cm s^{-1} is used for v in the simulations with different sink locations. This is a typical value for a reactive gas [15]. The dependence of the carbon burden on v of the sink is also shown in Fig. 1. Here, the loss of carbon is shown to be linear, as is expected by the nature of the deposition velocity driven sink.

The net loss ranges from 1 to 10 Gton C yr^{-1} for the single box locations and is 17 Gton C yr^{-1} for the two boxes in the Pacific (Table 4). The negative carbon flux is about 40 kton C km^{-2} yr^{-1} at all single locations (ranging from 37 to 42 kton C km^{-2} yr^{-1}) and 50 kton C km^{-2} yr^{-1} for the combined Pacific locations. On a per area basis, all the single locations are about the same in CO_2 absorption efficiency. Although the sink area is increased by 40% from the equatorial Pacific sink to the mid-latitude Pacific sinks, the net carbon loss increases by 70%. This may be due to low winds at the equator. The overall loss of CO_2 depends on v and the amount of CO_2 in the grid box, which, in turn, is controlled by the meteorology and losses. No sources are investigated here, but the location of sources and other sinks would also change the global mixing ratio distribution.

The surface mixing ratio (ppmv) of CO_2 is shown for the entire globe for each sink location after one year of loss (Fig. 2). These snapshots illustrate the CO_2 shadow that results from the sink. The deepest shadow is produced for the Gobi Desert sink. This may be due to high pressure or other meteorological events that would allow the air to become stagnant over the sink. To

Table 3
CO_2 uptake efficiency for various deposition velocities at the Nevada location

Deposition velocity (cm s^{-1})	Net loss (Gton C yr^{-1})
0.1	0.9
0.4	3.2
0.5	4.0
1.0	7.2
5.0	18.9
10.0	18.9

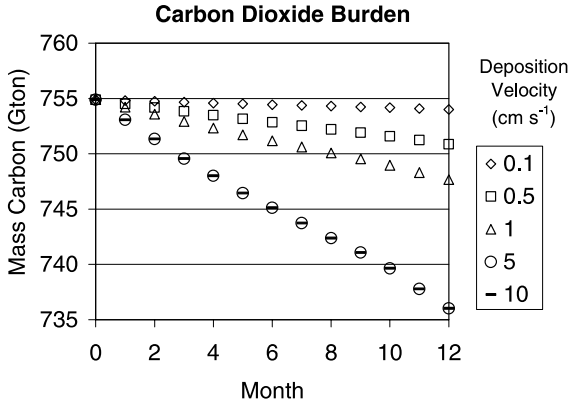

Fig. 1. The effect of deposition velocity on CO_2 burden (Gton C) for the Nevada box sink location.

Table 4
CO_2 uptake efficiencies with $v = 1$ cm s^{-1} at five locations

Location of sink	Longitude, latitude (mid-point)	Loss CO_2 (kton C km^{-2} yr^{-1})	Loss CO_2 (Gton C yr^{-1})
Antarctica	3°E, 82°S,	41.2	1.4
Gobi Desert	108°E, 50°N,	42.3	6.7
Nevada	118°W, 38°N	37.1	7.2
Equatorial Pacific Ocean	178°W, 2°S	40.8	10.1
NH + SH Pacific Ocean (two box)	178°W, 46°N + 46°S	49.9	17.2

further investigate this, the time series mixing ratio of CO_2 is monitored over one year (Fig. 3). The CO_2 mixing ratio in the Gobi Desert box fluctuates predominately between 250 and 350 ppmv, and spikes downward to 150 ppmv twice during the winter months of December and January. During the rest of the year, there appears to be a bimonthly drop in mixing ratio, but the average is 300 ppmv.

6. Discussion

The CTM results indicate that using a 4° × 5° sized deposition velocity sink with v of 0.5 cm s^{-1} or higher sequesters enough CO_2 to counteract the atmospheric increase of 3 Gton C yr^{-1}. For v of 1 cm s^{-1}, the average uptake at various locations is 40 kton C km^{-2} yr^{-1}. At this rate, a sink area of about 75,000 km^2 is needed to balance the increase. However, by using large numbers of active small units dispersed so that they don't see each other's CO_2 shadows, the active source area could be reduced by several orders of magnitude. The maximum amount of CO_2 absorbed above v of 5 cm s^{-1} is about 20 kton C yr^{-1}. The location of the sink is important in terms of the global CO_2 mixing ratio distribution and the resulting CO_2 shadow created. The fluctuation of CO_2 may have large impacts on the biosphere. However, this may compare to natural seasonal and diurnal fluctuations of CO_2. For example, in a forest, CO_2 concentrations can fluctuate from 305 ppmv

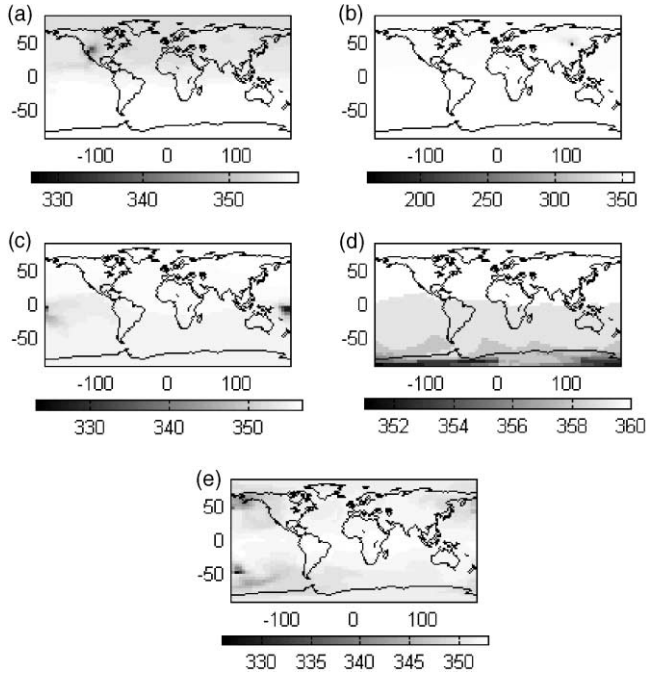

Fig. 2. CO_2 mixing ratio (ppmv) after one year of 1 $cm\,s^{-1}$ deposition velocity sink in the following locations: (a) Nevada, (b) Gobi Desert, (c) Equatorial Pacific Ocean, (d) Antarctica, (e) Northern and Southern Pacific Ocean.

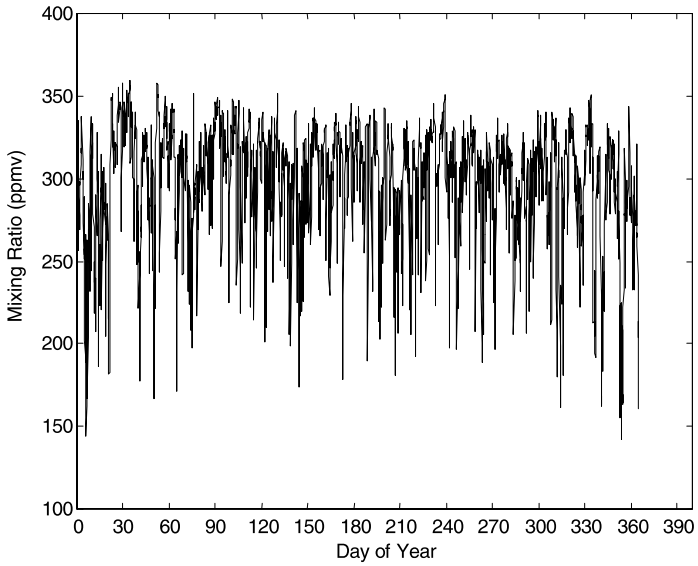

Fig. 3. Time series mixing ratio of CO_2 for one year at Gobi Desert location.

during peak photosynthetic activity (around noon) to 400 ppmv at night [27]. Also, CO_2 can vary seasonally up to 6 ppmv in certain locations, as evidenced from data in Mauna Loa, Hawaii [28]. High levels of CO_2 are observed in winter and spring, corresponding to low photosynthetic

activity. In addition, there is a gradient of CO_2 (4 ppmv) from the northern to the southern hemisphere, due mostly to the dominant use of fossil fuels in the northern hemisphere [29].

Photosynthesis is, thus, a comparable natural system to the engineered sink. The global net primary productivity (NPP) is 60×10 Gton C yr^{-1} [29]. The most efficient types of ecosystems in terms of mean NPP per area are wetlands (1.3 kg C m^{-2} yr^{-1}), forests (0.4–0.8 kg C m^{-2} yr^{-1}), cultivated land (0.8 kg C m^{-2} yr^{-1}) and tropical woodland and savanna (0.45 kg C m^{-2} yr^{-1}). One of the most efficient photosynthetic CO_2 absorbers is corn. At high illuminance and 300 ppmv ambient CO_2, the net photosynthetic capacity of single leaves is 40–55 kg CO_2 m^{-2} leaf yr^{-1} [30]. Using the relationship between v and CO_2 uptake at the Nevada location, v is estimated to be about 0.39 cm s^{-1}, resulting from the corn photosynthetic uptake above. If the Nevada location were covered with cornfields instead of a 1 cm s^{-1} perfect absorber, the photosynthetic uptake of CO_2 would be 60 kg C m^{-2} yr^{-1}, less than half the engineered sink uptake at 1 cm s^{-1}. This is probably an extremely high estimate, since laboratory studies tend to use optimal plant selections and environmental conditions. Also, this assumes 100% leaf cover and continuous lighting. A more practical estimate would be 5% or less (3 kg C m^{-2} yr^{-1}), which is still higher than wetlands and forests on a per area basis.

7. Conclusions

CTM calculations confirm earlier estimations [1] that a chemical sink, engineered correctly ($v >$ 0.5 cm s^{-1}), and placed in a large, remote geographical area such as Nevada or the Gobi Desert, could remove enough CO_2 annually to compensate for the atmospheric increase. A model chemical system of $Ca(OH)_2$ has promising thermodynamics for chemical sinkage, but the kinetics should be further investigated in the laboratory, as well as other scrubbers. The chemical sink was compared to photosynthetic sinks and could surpass their carbon uptake, given $v > 1$ cm s^{-1}. Building the engineered sink upward would facilitate mixing and increase the effectiveness of CO_2 uptake. Other factors must be considered, such as economics and limiting resources, that could restrain such creation of a chemically engineered CO_2 sink. Risk assessment must also be considered regarding the CO_2 shadow created. However, given ideal thermodynamics and kinetics, the meteorology is sufficient to reduce the amount of atmospheric CO_2, or at least keep it from increasing.

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